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COMPLETE SPECIFICATION

A Process for Improving the Adhesion of Fibrous Materials to Rubber

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coating compositions for natural or synthetic fibrous materials, such as cotton, viscose rayon and nylon, to improve the adhesion thereof to rubber such as natural rubber or especially synthetic rubber such as GR-S rubber, Buna-N rubber, (the word "Buna" is a Registered Trade Mark), and preferably butyl rubber.

More particularly the present invention relates to coating fibers, filaments, or especially tire cords with a first layer of a phenolic-aldehyde resin-containing rubber latex, and then with a brominated butyl rubber cement and drying and the invention further relates to incorporating the thus treated fibers, filaments or cords into a rubber matrix to form a composite such as the carcass plies in tires.

The present invention therefore comprises a process for improving the surface adhesion of a fibrous material comprising coating said material with a phenolic-aldehyde resin-containing rubber latex other than a butadiene styrene-vinyl pyridine latex and then with a brominated butyl rubber, containing sufficient amounts of bromine, to improve its adhesion characteristics, and drying.

In another aspect the present invention comprises a process for the production of a laminated structure comprising embedding the phenolic-aldehyde resin-containing latex and brominated butyl rubber coated fibrous material in an unvulcanised rubber matrix and vulcanizing *in situ* at an elevated temperature.

Heretofore, natural and synthetic fibers such as cotton, viscose rayon and nylon threads, cords, or filaments have adhered very poorly to rubber and to compounded rubber stocks (especially containing butyl rubber) when they were united and the rubber stock subsequently cured according to any known process of producing adhesion between rubber and fibers. This poor adhesion, especially of synthetic threads, cords, and 55 fabrics to synthetic rubber such as butyl rubber has constituted a very serious obstacle to more extensive use of butyl rubber in the manufacture of automobile tires, reinforced rubber belts and similar products consisting 60 of alternate plies of rubber and cords. Such products are required to adhere very strongly for long periods of time under drastic conditions of high temperature, constant flexing, bending and shock. For example, 65 if nylon cord is pressed into butyl rubber or a butyl rubber stock and the composite vulcanized, it will be observed that the nylon cord may be pulled away from the rubber with comparative facility. 70

Butyl rubber comprises a copolymer containing 85 to 99.5%, preferably 95 to 99.5% of a C₄ to C₈ isoolefin such as isobutylene, the remainder being a C₄ to C₁₀ multi-olefin, preferably a C₄ to C₆ conjugated 75 diolefin such as butadiene, dimethyl butadiene, piperylene or especially isoprene. The preparation of butyl-type rubbers is described in British Specification No. 565,974 and also in other patents as well as in litera- 80 ture.

According to the preferred form of the present invention, fibrous materials such as tire cords are coated with a phenolic-aldehyde resin-containing rubber latex having 1 to 25 85 weight percent and particularly preferably 5 to 20 weight percent rubber latex solids, 0.1 to 5.0 weight percent, particularly preferably 0.4 to 3.0 weight percent of the phenolic material, preferably resorcinol, 0.2 to 3.0 90

weight percent, particularly preferably 0.3 to 1.5 weight percent of the aldehyde, preferably formaldehyde, and 70 to 95 weight percent, particularly preferably 75 to 90 weight percent water. Before coating, the phenolic-aldehyde resin-containing rubber latex is advantageously adjusted to a pH of between 7 and 13, preferably 8 to 11 and aged at 40° to 150°F., preferably at 50° to 100°F. for a time, depending upon the temperature, of 20 minutes to 30 hours, preferably 1 to 20 hours and the fibrous materials coated with the thus aged latex. The latex-coated fibrous materials are then dried, preferably with slight or substantial stretching depending upon the particular fiber and use contemplated for 0.05 to 30 minutes, preferably 0.1 to 10 minutes at 200° to 550°F., preferably 250° to 480°F., principally to at least partially thermoset the resin, drive off volatile materials and, if necessary, stretch the fiber.

The resulting dried coated fibrous materials, such as tire cords, are then dipped or treated with a brominated butyl rubber cement having, per 100 parts by weight of brominated butyl rubber, 5 to 150, advantageously 10 to 120, and preferably 15 to 90 parts by weight of a filler such as silica, clays, alumina, diatomaceous earth, calcium carbonate, silica-alumina, and preferably carbon black with or without the addition of conventional curatives such as sulfur, zinc oxide, derivatives of thiuram or carbamic acid, quinoid compounds, mono- or poly-functional amines, phenol-dialcohol resins of the polymethylol phenol type, benzothiazyl disulfide, mercaptobenzothiazole, mercapto imidazoline and sulfanomides. The brominated butyl rubber cement generally contains 5 to 25 weight percent, preferably 10 to 20 weight percent solids in a C₅ to C₁₀ hydrocarbon such as pentane, hexane, isooctane, cyclohexane, methyl cyclohexane, benzene, toluene, naphthas or mineral spirits, or a halogenated hydrocarbon such as ethylene dichloride, chloroform or carbon tetrachloride.

The treated fibrous material is then dried to remove the hydrocarbon solvent at 150° to 300°F., preferably 200° to 250°F., for 0.5 to 30 minutes, preferably 1 to 10 minutes, preferably under conditions of extended storage. However, air drying at room temperature will suffice. The dried treated fibrous materials such as tire cords are then imbedded as by calendering in an unvulcanized rubber matrix such as natural rubber, butyl rubber, chlorinated butyl rubber, brominated butyl rubber, neoprene rubber, GR-S rubber, Buna-N rubber, rubbery vinyl pyridine-butadiene copolymers and rubbery tripolymers of butadiene-acrylonitrile-vinyl pyridine and vulcanized *in situ* for 0.5 to 90 minutes at 200° to 450°F. to produce a finished article having an improved bond between the coated fibrous material and

rubber.

The above procedure produces superior articles suitable for use in constructing tire carcasses for automobiles, trucks and airplanes, as well as numerous other uses such as conveyor belts, transmission belting, rubber hosing e.g. steam hose air springs and other products built up of a plurality of laminations of cord and rubber, the invention being especially applicable to such products which have at least one layer which is of butyl rubber. The invention may also be applied in uses involving merely a single layer of a fabric such as nylon, cotton, viscose rayon and silk, which may be either coated on one side or both sides, with the resin-containing rubber latex and brominated butyl rubber cements as described above.

Among the rubber latices which may be used in the practice of this invention are butyl rubber latex, natural rubber latex and polyhaloalkadiene rubber latex. The butyl rubber latex is prepared by dissolving butyl rubber in a hydrocarbon solution, preferably in an aliphatic hydrocarbon of 6 to 8 carbon atoms, e.g. hexane. The hydrocarbon solution may then be emulsified with water in accordance with conventional methods.

The emulsifiers preferably used belong in general to non-ionic, anionic and cationic types. The non-ionic emulsifiers found useful are the polyoxyalkylated alkyl phenols or alcohols having the formula R(OCHR₁CHR₁)_nOH, where R is a C₁ to C₁₈ alkyl, aryl, aralkyl or alkaryl group; R₁ is C₁ to C₁₀ alkyl group or hydrogen and n is an integer of 2 to 12, or especially 4 to 8. The alkylene oxide units should represent at least 20% and preferably at least 40% of the total molecular weight of the compound. These compounds are prepared by condensing an alkyl phenol or an alcohol with an alkylene oxide such as ethylene oxide or propylene oxide. Commercial compounds which have been found useful in connection with the present invention include such polyoxyethylated alkyl phenols as Triton X-100, (The word "Triton" is a Registered Trade Mark) Triton X-45, and Igepal CO-430 or polypropylene glycol-ethylene oxide condensation products such as Pluronic F-68.

The anionic emulsifiers useful for the purposes of the present invention include sodium lauryl sulfate, the sodium salt of the sulfonates of the polyoxyethylated alkyl phenols, and sodium oleyl taurate.

The cationic emulsifiers useful in combination include the alkyl dimethyl benzyl ammonium chlorides, diisobutyl phenoxy-ethoxyethyl dimethyl benzyl ammonium chloride and dimethyl phenoxy-ethoxyethyl dimethyl benzyl ammonium chloride.

A particularly suitable anionic emulsifier consists of a fatty acid soap of an alkali

metal, e.g. sodium oleate or potassium oleate or the corresponding palmitates and stearates. The emulsifier may be formed *in situ* by adding the acid to the solution of butyl rubber 5 in the hydrocarbon and then adding a dilute aqueous hydroxide or carbonate solution to form the emulsion.

A very effective emulsifier which produces excellent butyl rubber latices having good 10 mechanical and chemical stability consists of a mixture of about 5 to 15 (e.g. 10) parts of a polyoxyethylated octyl phenol containing 8 to 10 (e.g. 9) ethylene oxide units, and available commercially as Triton X-100, 15 with 0.5 to 5.0 (e.g. 1.0) parts of sodium lauryl sulfate. Instead of Triton X-100, a polypropylene glycol-ethylene oxide condensation product may be used in which the ethylene oxide units represent about 80 20 to 90% (e.g. 85%) of the molecular weight and in which the polypropylene glycol has an actual molecular weight of 1500 to 1800 (e.g. 1650) and which is known under the trade name Pluronic F-68.

25 Another excellent emulsifier is an equal mixture of Igepon TK-42, Triton X-100 and a polyoxyethylated nonyl phenol having 43% of its molecular weight present as ethylene oxide units (equivalent to 4 ethylene 30 oxide units) and known as Igepal Co-430. The first of the non-ionic emulsifiers mentioned is soluble in the water while the latter is soluble in the hydrocarbon. By using these along with the Igepon TK-42 troubles due to 35 foaming, if encountered when sodium lauryl sulfate is used, are overcome. Sodium lauryl sulfate generally produces a more stable latex and may be added to the system after the processing operations are complete if 40 desired.

The initial amount of emulsifier to be used may vary but a desirable amount is enough to leave less than 10.0 weight percent and preferably less than 5.0 weight percent based 45 on polymer, in the final latex. During creaming, about one-third to one-half of the emulsifier is removed. For this reason about 10 to 25 weight percent emulsifier based on polymer is advantageously used. How- 50 ever, from about 5 to 30% emulsifier based on polymer may be used, if desired. Adhesion to tire cords is improved by keeping the concentration below 15%, preferably below 10%.

55 After preparation of the emulsion, the hydrocarbon solvent is removed by stripping. Foaming during this step can be reduced by diluting the latex with stripped or partially stripped latex during the stripping operation.

60 If desired, however, the foam may be allowed to carry the solvent over in a gaseous state to a cooling surface where the solvent condenses and the foam breaks, leaving an aqueous layer under a liquid solvent layer.

65 These layers are then separated.

Butyl rubber latex may also be prepared with highly efficient mixing equipment, i.e., colloidal mills or sonic mixers wherein considerably less total emulsifier may be used without creaming as described above. 70 A protective colloid agent, such as polyvinyl alcohol, may also be added in order to minimize coagulation.

The natural rubber latex used may be obtained as "normal latex", centrifuge-75 concentrated natural latex, creamed-concentrated natural latex, evaporation-concentrated natural latex, electrodecantation-concentrated natural latex or any other form of natural rubber latex commercially available and 80 known in the art as Hevea latex such as Hevea Brasiliensis latex. The natural rubber latex used in the examples given hereinafter is a heat concentrated natural rubber latex which has been concentrated after the addi- 85 tion of soap and caustic according to the Revertex process as described in British Specification No. 243,016 known as "Revertex" (The word "Revertex" is a Registered Trade Mark) and containing 72 weight per- 90 cent solids and having a dry rubber content of 67% by weight a specific gravity of 0.97 and a density of 8.1 pounds per gallon.

The polyhaloalkadiene rubbers, useful for the purposes of the present invention, 95 include among others, poly-2-halo-alkadienes having 4 to 18 carbon atoms as the monomeric unit in the polymerization chain. Poly-2-chloro-alkadienes-1,3 and poly-2-bromo-alkadienes-1,3 known in the art as polychloro- 100 prenes and polybromoprenes, respectively, are preferred. The most preferred polyhalo-alkadiene rubbers are poly-1-alkyl-2-bromo-1,3-butadiene; poly-1-alkyl-2-chloro-1,3-butadiene; poly-2-bromo-1,3-butadiene, and 105 especially poly-2-chloro-1,3-butadiene.

In the preparation of the fiber-treating dispersions, latices such as those described above are mixed, in accordance with the present invention, with a phenolic compound 110 and an aldehyde which are capable of condensing or polymerizing *in situ* to form a heat-hardening phenolic-aldehyde resin. Since the presence of alkalies such as sodium and potassium hydroxide catalyzes the 115 polymerization or condensation of the phenol and the aldehyde to form the resin, these may be present in the dispersion together with the latex, the phenol and the aldehyde. A solution of resorcinol, formaldehyde and 120 caustic may be aged for about 2 to 20 hours prior to mixing with the latex or, as above described, the ageing may take place after mixing with the latex.

The latex may be mixed with a phenol 125 formaldehyde solution such as an aqueous solution containing resorcinol and formaldehyde in accordance, for example, with the following recipe:

5 to 25% latex solids

130

0.5 to 5.0% resorcinol
1.0 to 10.0% of 37% formaldehyde
60 to 93.5% water

Before use, the pH of the mixture is adjusted, i.e. by titration with an alkali such as sodium hydroxide to between 7.5 and 9 and the mixture is allowed to stand until condensation of the phenol and formaldehyde occurs, preferably overnight.

10 It has been observed that the pH of the latex-resorcinol-formaldehyde mix changes considerably after standing. When the original adjusted pH is below 8.5 to 8.7 the pH after ageing overnight is found to have decreased, while if the original adjusted pH is above 8.5 to 8.7 the aged pH will have increased.

The phenolic-aldehyde resins which are within the purview of the present invention may be generally defined as belonging to the class of heat-hardening phenol-aldehyde type resins, preferably resins from phenolic compounds which, prior to heat-hardening or thermosetting are water soluble at least to the extent of 5 to 10% or more. Such resins are capable of thermally setting in the absence of any added catalysts at temperatures of about 150° to 400°F., temperatures of 200° to 250°F. being preferred for coating viscose rayon whereas higher temperatures are permissible for nylon.

As phenolic compounds capable of producing resins of the above-mentioned characteristics, mono or especially polyhydroxy benzenes are satisfactory. Di-hydroxy benzenes having the hydroxyl groups meta with respect to each other are preferred. Satisfactory phenolic compounds include phenol, cresols, phloroglucinol, xylenols, trimethyl phenols, mono or dichloro phenols, diamyl or diisopropyl phenols, p-tertiary butyl phenol, p-phenol-phenol, hydroquinone, and especially resorcinol.

The preferred aldehydes for reaction with the above phenolic compounds include formaldehyde or a material supplying formaldehyde such as paraformaldehyde. Other suitable aldehydes include acetaldehyde, propionaldehyde and furfural. The ratio of the phenolic compound to the aldehyde is preferably such that the resin, prior to thermosetting, has substantial water solubility as well as solubility in polar solvents. In order to produce the desired resin, a small amount of an alkali metal containing catalyst or other condensing agent is preferred. If sodium hydroxide is employed, it is advantageously present in amounts of 0.02 to 0.5 percent by weight, based on reactants.

60 The brominated butyl rubber is produced by reacting the unvulcanized rubber *per se* or dissolved in a solvent with bromine or bromine-liberating compounds so that the polymer contains at least 0.5 weight percent of combined bromine but not more than

3 atoms of bromine combined in the polymer per molecule of multiolefin present therein; i.e. not more than 3 atoms of combined bromine per double bond in the polymer.

Suitable brominating agents which may be employed are molecular bromine, alkali metal bromides (preferably sodium hypobromite), sulfur bromides (particularly oxygenated sulfur bromides), N-bromo-succinimide, N,N'-dibromo dimethyl hydantoin, alpha-bromoaceto acetanilide, N-bromoacetamide and beta-bromo-ethyl phthalimide. The preferred brominating agents are molecular bromine and/or those bromine compounds which are known to lead to allylic substitution, e.g. N,N'-dibromo dimethyl hydantoin, N-bromosuccinimide, beta-bromoethyl phthalimide and N-bromoacetamide. The bromination is advantageously conducted at -30°C. to +200°C., preferably at 20° to 170°C. for about one minute to several hours. However, the temperatures and times are regulated to brominate the rubbery copolymer to the extent above mentioned.

The bromination may be accomplished 90 in various ways. One process comprises preparing a solution of the copolymer as above, in a suitable inert liquid organic solvent such as an inert hydrocarbon or advantageously halogenated derivatives of 95 saturated hydrocarbons, examples of which are hexane, heptane, naphtha, kerosene, straight run mineral spirits, benzene, toluene, chlorobenzene, chloroform, trichloroethane and carbon tetrachloride, and adding thereto 100 the bromine or other brominating agent, optionally in solution, such as dissolved in an alkyl chloride, e.g. carbon tetrachloride.

Another variation comprises employing liquid bromine. Still a further method resides 105 in blending with the solid copolymer a solid brominating agent which is known to lead to allylic substitution such as N,N'-dimethyl dibromo hydantoin or N-bromosuccinimide, supra. In such a case, the blend formed is preferably mill-mixed and heated to a 110 temperature sufficient to brominate the solid copolymer. The use of elevated or reduced pressures is optional since atmospheric pressure is satisfactory. However, the pressure may vary, depending upon the foregoing 115 temperatures and reaction times from about 1 to 400 p.s.i.a.

The invention will be better understood from the following experimental data. 120

EXAMPLE I

Butyl latex was prepared according to the following formulation:

LATEX A

3.4 phr* potassium oleate 125
2.4 phr* Triton X-100
2.4 phr* polyvinyl alcohol (80% hydrolyzed)
* parts per 100 parts dry rubber.

A 30 weight percent solution of butyl rubber in hexane was prepared and 3.0 phr 130

of oleic acid was mixed in. An equal volume of water containing 2.4 phr Triton X-100; 2.4 phr polyvinyl alcohol; 0.6 phr potassium hydroxide was also prepared and fed together with the butyl rubber solution to a highly efficient mixing machine known as a Rapisonic Homogenizer, and recycled 4 times. The resultant latex was stripped of hexane and water to a total solids content of 35 weight percent.

EXAMPLE II

Nylon tire cords were dipped at room temperature in the above butyl rubber latex containing a resorcinol-formaldehyde blend in accordance with the following formulation:

Component	Parts by weight
Butyl rubber latex solids	15
Resorcinol	2.5
Formaldehyde (37%)	3.5
Water	79.3

The solution containing resorcinol and formaldehyde in water was added to the latex and the pH adjusted to 8.3 with 10 weight percent caustic solution. The total mix was aged at 70°F. for 16 hours. The nylon cord, after dipping in the above formulation, was then dried at 425°F. for 0.9 minutes. This treated cord was then dipped at room temperature into a brominated butyl rubber cement having 15 weight percent solids wherein the brominated butyl rubber had a viscosity average molecular weight of 360,000, a mole percent unsaturation of 0.6, a Mooney viscosity (8 minutes at 212°F.) of 53, and 2.45 weight percent combined bromine.

For comparison purposes, a portion of the resin containing butyl rubber latex treated cord was dipped in an unbrominated butyl rubber cement having 15 weight percent solids, wherein the unbrominated butyl rubber had a viscosity average molecular weight of 496,000, a Mooney viscosity (8 minutes at 212°F.) of 71 and a mole percent unsaturation of 1.4.

In both instances, i.e. in the process according to the present invention employing brominated butyl rubber cement and in the comparative test with a non-brominated butyl rubber cement, the solids portion of the cement had the following composition wherein the compounded stock had been milled on a rubber mill at room temperature for 15 minutes.

Component	Parts by weight
Polymer	100
Carbon Black (MPC)	50
Zinc Oxide	5.0
*p-octyl phenol-formaldehyde heat reactive resin containing 6% methylol groups (Amberol ST-137)	as shown below

* The p-octyl-phenol-formaldehyde resin was added to both compositions in runs 2, 3, 4 and 5 below and the same resin, but brominated to contain 3.5 wt.% bromine, was added in runs 6, 7 and 8 below. The brominated resin was obtained by reacting the phenol-formaldehyde resin with hydrogen bromide.

The cords, double coated as above, were then each dried for 2 minutes at 250°F. The cords were then lodged in an uncured butyl rubber matrix and vulcanized for 25 minutes at 320°F.; the matrix having the following composition:

Ingredient	Parts by weight	
Butyl rubber**	100	
MPC carbon black	24	
SRF carbon black	16	85
N-nitroso-p-nitroso methyl aniline	1.0	
Zinc oxide	5.0	
Sulfur	2.0	
Tellurium diethyl dithiocarbamate	1.25	90
Plasticizer hydrocarbon oil oil "A" *	12.5	

* The plasticizer hydrocarbon oil was a paraffinic base oil having the following characteristics:

Aniline Point (°F.)	215	
S.S.U. at 100°F.	508	100
S.S.U. at 210°F.	58	
Pour Point (°F.)	30	
Flash Point (°F.)	365	
Specific gravity	0.90	

** The butyl rubber of the matrix had a viscosity average molecular weight of 336,000, a mole percent unsaturation of 1.99, and a Mooney viscosity (212°F. for 8 minutes) of 45.

The adhesions of the cords, coated in accordance with the invention, to the matrix were measured by a technique essentially similar to the "H" test described by Lyons, Conrad and Nelson, Rubber Chemistry and Technology, 268, Vol. XX (1947). The tire cords used were nylon tire cords of 840 denier 2 ply construction. The test specimens were prepared with a $\frac{3}{8}$ inch length of treated cord vulcanized into the center of a $1\frac{1}{2} \times \frac{3}{8} \times \frac{1}{8}$ inch butyl rubber matrix composition. The vulcanized rubber matrix was reinforced with light cotton duck on the two long sides from which the cord did not protrude. The force required to pull the $\frac{3}{8}$ inch length of cord from the rubber block was measured by means of a Scott Tensile Tester at 10 inches per minute jaw separation rate at 70°F.

		"H" TEST ADHESIONS (lbs/end)			
Run No.		Amount of p-octyl- phenol-formaldehyde resin present	Amount brominated p- octyl-phenol-formaldehyde resin present	Non-brominated butyl dip	Brominated butyl dip
5	1	—	—	7.3	14.7
	2	2	—	6.9	14.7
	3	4	—	6.8	14.0
	4	8	—	6.7	14.4
	5	16	—	6.7	12.5
10	6		4	6.5	14.2
	7		8	6.3	13.5
	8		10	6.4	13.2

The data above indicate that superior adhesion is obtained when employing the brominated butyl rubber cement in accordance with the present invention than when employing unbrominated butyl rubber. The data also show that addition of a further resin which in three runs was a brominated resin did not appreciably effect the results.

EXAMPLE III

Nylon tire cords (type T-300) were dipped at room temperature in a resin-containing natural rubber latex of the following formulation:

Component	Parts by weight
Revertex latex solids	15
Resorcinol	1.1
Formaldehyde (37%)	1.9
Water	82

The solution containing resorcinol and formaldehyde in water was aged for six hours at room temperature (75°F.) after adjustment of the pH to 9.5 with 10% caustic solution and then blended with the latex at which time the pH rose to 10.2. The nylon cord, after dipping in the above formulation, was then dried at 250°F. for 5 minutes. This treated cord was then dipped at room temperature into a brominated butyl rubber cement having 15 weight percent solids wherein the brominated butyl rubber had a viscosity average molecular weight of 360,000, a mole percent unsaturation of 0.6, a Mooney viscosity (8 minutes at 212°F.) of 53, and 2.45 weight per cent combined bromine. For comparison purposes, a portion of the resin-containing natural rubber latex treated cord was dipped in an unmodified butyl rubber latex cement having 15 weight per cent solids, wherein the unmodified butyl rubber had a viscosity average molecular weight of 496,000, a Mooney viscosity (8 minutes at 212°F.) of 71 and a mole percent unsaturation of 1.4. In each run, i.e. in the brominated butyl run and in the unbrominated butyl run the solids portion of the cement had the following composition in the preparation of which the compounded stock had been milled on a rubber mill at room temperature for 15 minutes:

Component	Parts by weight
Polymer	100
Carbon black (MPC)	50
Zinc Oxide	5.0
p-octyl phenol-formaldehyde heat reactive resin containing 6% methylol groups (Amberol ST-137)	8.0

The cords, double coated as above, were then each dried for 2 minutes at 250°F. The cords were then lodged in an uncured butyl rubber matrix and vulcanized for 25 minutes at 320°F.; the matrix having the following composition:

Ingredient	Parts by weight
Butyl rubber**	100
MPC carbon black	24
SRF carbon black	16
N-nitroso-p-nitroso methyl aniline	1.0
Zinc oxide	5.0
Amberol ST-137X(a)	2.5
Sulfur	2.0
Tellurium diethyl dithiocarbamate	1.25
*Plasticizer hydrocarbon oil "A"	12.5
* The plasticizer hydrocarbon oil was a paraffinic base oil having the following characteristics:	
Aniline Point (°F.)	215
S.S.U. at 100°F.	508
S.S.U. at 210°F.	58
Pour point (°F.)	30
Flash point (°F.)	365
Specific gravity	0.90
** The butyl rubber of the matrix had a viscosity average molecular weight of 336,000, a mole percent unsaturation of 1.99, and a Mooney viscosity (212°F. for 8 minutes) of 45.	

(a) Non-reactive p-octyl phenol-formaldehyde resin.

The adhesions of the cords, coated in accordance with the invention, to the matrix were measured as described above. The results were as follows:

"H" TEST ADHESION RESULTS (Adhesion in pounds at room temperature)	
Brominated butyl rubber cement	16.5
Unmodified butyl rubber	8.8

The above data indicates that superior adhesion is obtained when employing the brominated butyl rubber cement in conjunction with a resorcinol-formaldehyde resin-containing natural rubber latex in accordance with the present invention.

EXAMPLE IV

Nylon tire cord of 840 denier/2 ply construction (T-300) was treated with a resin-containing natural rubber latex dip as in Example III and dried as described in Example III. The brominated butyl rubber, the same as that described in Example III, was compounded on a cool 12 inch laboratory

mill to prepare the compositions shown below. Cements were prepared by adding 15 g. of each to 85 g. of hexane and agitating on a mechanical shaker for 16 hours. Nylon cord lengths, treated and dried as described above with a natural rubber latex composition, were dipped in one of the cements and dried for 2 minutes at 250°F. Adhesion test specimens were prepared using the rubber matrix formulation and vulcanization procedure of Example III. The forces required to dislodge the $\frac{3}{8}$ inch lengths of imbedded cord as measured by a Scott Tensile Tester were as follows:

30	Cement Compound Composition (Parts by Weight)				" H " Test Adhesion (Pounds)	30
	Brominated Butyl Rubber	Carbon Black (MPC)	Zinc Oxide	Amberol ST-137		
	100	—	—	—	11.0	
35	100	50	—	—	18.1	35
	100	50	5	—	15.4	
	100	50	5	8	16.0	

The above data show that good adhesion is not dependent on the presence of resin (Amberol ST-137) or zinc oxide but that a filler such as carbon black is an essential component.

EXAMPLE V

Nylon tire cord was treated with a resin-natural rubber latex dip and dried as in Examples III and IV. The brominated butyl rubber of Example III was compounded

on a laboratory mill with varying amounts of filler, as indicated below, and brominated butyl rubber cements prepared in hexane at 15% solids as described in Example IV. The latex treated cord was dipped in one of the following brominated butyl rubber cements, dried and adhesion samples prepared and tested as in Examples III and IV with the following results:

60	Cement Compound Formulation (Parts by Weight)		" H " Test Adhesion (Lbs. @ 75°F.)	60
	Brominated Butyl Rubber	Carbon Black (MPC)		
	100	70	18.0	
	100	50	18.5	
	100	25	18.6	
	100	10	17.2	
	100	0	11.0	

The above data show that, with as little as 10 parts per hundred of brominated butyl rubber of a reinforcing filler (e.g. carbon black) present in the cement composition, excellent adhesion between the butyl rubber matrix and nylon cord is realized. The data further show that increasing the amount of added filler up to 70 parts per hundred of brominated butyl rubber gives about the same adhesion as when using only 10 parts of added filler. This indicates that the amount of filler may be varied over a broad range and yet result in the improvements of the present invention.

EXAMPLE VI

Nylon tire cord was given a first treatment with a natural rubber latex-resin system as

described in previous examples. A portion of this coated and dried cord was then dipped in one of the following 15% solids in hexane cements wherein the bromine content of the polymer compounded with 50 p.h.r. of carbon black (MPC) was varied. After application of the cement coating, the cords were dried for 2 minutes at 250°F. and " H " test samples prepared and tested as in Example III. The adhesion values, obtained between nylon cord and the butyl rubber matrix of Example III using this double coated cord, wherein the bromine content of the brominated butyl rubber cement varied from 0.17% to 2.45%, are shown in the following table.

<i>Brominated Butyl Rubber Employed</i>			<i>"H" Test Adhesion</i> (Lbs. at 75°F.)	
<i>Bromine Content</i>	<i>Iodine No. (a)</i>	<i>Intrinsic Viscosity(b)</i>		
0.17%	9.7	1.58	10.7	5
0.43%	8.3	1.49	15.4	
1.38%	7.4	1.74	18.2	
2.45%	4.1	1.11	18.9	
(a) Drastic Iodine Mercuric Acetate Method—Gallo & Weise, Industrial and Engineering Chemistry, Vol. 40, 1277 (1948).				
10	(b) Intrinsic viscosity in diisobutylene at 25°C.			10

The above data indicate that a reduction of the bromine content below about 0.4% will result in a less efficient bonding system.

EXAMPLE VII

Using the brominated butyl rubber of Example III containing 2.45% bromine, a cement was prepared at 15% solids in hexane from a brominated butyl rubber compound which was prepared on a cool laboratory mill in the formulation: polymer—100 parts and carbon black (MPC)—50 p.h.r. This cement was applied to nylon tire cord dipped in one of the latex formulations described in the following table, dried for 5 minutes at 250°F. and "H" test adhesion specimens prepared as described in Example III after drying the brominated butyl rubber cement coating by placing the double coated cord in

an air oven for 2 minutes at 250°F.

The latex dips were prepared by dissolving the formaldehyde and resorcinol in the dip make-up water and slowly adding this resorcinol-formaldehyde solution to the natural rubber latex with gentle agitation. The pH of the newly completed dip was then adjusted from about 7.8 to about 8.3 by the addition of a minor concentration of a 10% sodium hydroxide solution. The resin was allowed to partially form by ageing this composition for 16 hours at 75°F. prior to treating the nylon tire cord. The adhesion results, obtained over a wide concentration range of resin-forming constituents in the natural rubber latex dip, are shown in the following table.

Parts By Weight (Unless Otherwise Indicated)					
Latex Formula	A	B	C	D	
Percent of Added Resin Reactants Based on					
Latex Solids	24.1%	12.0	5.9%	2.9%	50
Natural Rubber Latex Solids	15.0	15.0	15.0	15.0	
Resorcinol	2.2	1.1	0.55	0.27	
Formaldehyde, 37%	3.8	1.9	0.9	0.45	
Water	79.0	82.0	83.6	84.3	
(pH Adjusted to 8.3—Dips Aged for 16 Hours before Treating Nylon Cord; "H" Test Adhesion to Butyl Rubber Matrix—Double Coated Cord; lbs. @ 75°F.)					55
	19.7	20.1	20.4	14.9	

The above data indicate that good adhesion to nylon tire cord is obtained over the range of resin reactant contents from 2.9 to 24% based on rubber solids in the latex dip. The optimum range of resin contents, based on rubber solids, is between 5 and 25% of resin reactants based on latex rubber solids.

EXAMPLE VIII

Using latex formula B of Example VII, but differing only in stabilization with ammonia, for the preliminary coating of rayon tire cord, 1650 denier/2 ply construction, followed by a treatment with the 15% brominated butyl rubber cement of Example VII, an "H" test adhesion value of 24.2 pounds was obtained at 75°F. In this experiment after 16 hours ageing, the pH of the dip was increased to 10 by the addition of a minor concentration of 28.7% ammonia. This dip was shelf aged at 75°F. for 96 hours prior to treating the rayon cord. The latex treated rayon was dried for 5 minutes at

250°F., treated with brominated butyl rubber cement redried for 2 minutes at 250°F. and "H" test adhesion samples prepared as described in Example III. The "H" test adhesion value of 24.2 pounds obtained is in excess of known commercial requirements.

EXAMPLE IX

Nylon tire cords (840 denier/2 ply) were dipped at room temperature in a resin-containing Neoprene rubber latex of the following formulation:

Component	Parts by weight	
* Neoprene latex (36% solids)	14.0	95
Resorcinol	0.4	
Formaldehyde (37%)	0.6	
Additional Water	85	

* The Neoprene latex employed was type 735 consisting of poly-2-chloro-1,3-butadiene and having a specific gravity of 1.08, an initial pH of 12.2, and containing as the emulsifier the sodium salt of disproportionated rosin.

The solution containing resorcinol and formaldehyde in water was blended with the latex and the pH adjusted to 8.5 with 10% NaOH and aged for 16 hours at 75°F. The 5 nylon cord, after dipping in the above formulation, was then dried at 250°F. for 5 minutes. This treated cord was then dipped at room temperature into a brominated butyl rubber cement having 15 weight 10 percent solids wherein the brominated butyl rubber had a viscosity average molecular weight of 350,000, a mole percent unsaturation of 0.77, a Mooney viscosity (8 minutes at 212°F.) of 54, and 2.08 weight percent 15 combined bromine. For comparison purposes, a portion of the resin-containing natural rubber latex treated cord was not dipped in the brominated butyl rubber cement before use. The solids portion of 20 the brominated butyl rubber cement had the following composition in the preparation of which the compounded stock had been milled on a rubber mill at room temperature for 15 minutes:

25	<i>Component</i>	<i>Parts by weight</i>
	Polymer	100
	Carbon black (MPC)	50

The cords, coated as above, were then each dried for 2 minutes at 250°F. The 30 cords were then lodged in an uncured butyl rubber matrix and vulcanized for 25 minutes at 320°F.; the matrix having the following composition:

	<i>Ingredient</i>	<i>Parts by weight</i>
35	Butyl rubber**	100
	MPC carbon black	24
	SRF carbon black	16
	N-nitroso-p-nitroso methyl aniline	1.0
40	Zinc oxide	5.0
	Amberol ST-137X(a)	2.5
	Sulfur	2.0
	Tellurium diethyl dithiocarbamate	1.25
45	* Plasticizer hydrocarbon oil "A"	12.5
	* The plasticizer hydrocarbon oil was a paraffinic base oil having the following characteristics:	
50	Aniline Point (°F.)	215
	S.S.U. at 100°F.	508
	S.S.U. at 210°F.	58
	Pour point (°F.)	30
	Flash point (°F.)	365
55	Specific gravity	0.90

** The butyl rubber of the matrix had a viscosity average molecular weight of 336,000, a mole percent unsaturation of 1.99, and a Mooney viscosity (212°F. for 8 minutes) of 45.

(a) Non-reactive p-octyl phenol-formaldehyde resin.

The adhesions of the cords, coated in accordance with the invention, to the matrix 65 were measured as described above. The

results were as follows:

"H" TEST ADHESION RESULTS

(Adhesion in pounds at room temperature)

Brominated butyl rubber cement	19.4
No brominated butyl rubber cement	6.5 70

The above data indicates that superior adhesion is obtained when employing the brominated butyl rubber cement in conjunction with a resorcinol-formaldehyde resin-containing Neoprene rubber latex in 75 accordance with the present invention.

EXAMPLE X

The same general procedure as in Example IX was repeated substituting for the Neoprene rubber latex the following: 80

<i>Component</i>	<i>Parts by weight</i>	
Neoprene Latex type 735		
(36% solids)	43	
Resorcinol	1.1	
Formaldehyde (37%)	1.8	85
Additional Water	54.1	

Upon coating the cords with the aged resin-containing Neoprene Latex, drying and coating with the brominated butyl rubber cement as in Example IX, the following "H" 90 test adhesion results were obtained:

<i>Adhesion in pounds at room temperature</i>	
Brominated Butyl Rubber Cement	19.5
No Brominated Butyl Rubber Cement	7.0

The same general comments apply to the 95 results of this data as in Example IX.

One particularly advantageous use for the adhesion combinations of the present invention is pneumatic tires of either the inner tube containing variety or in tubeless type 100 tires.

The expression "layer" as employed in the claims is intended to include plies and liners, as well as such layers as the carcass, sidewalls and tread area of tires. 105

WHAT WE CLAIM IS:—

1. A process for improving the surface adhesion of a fibrous material comprising coating said material with a phenolic-aldehyde resin-containing rubber latex other 110 than a butadiene styrene-vinyl pyridine latex and then with a brominated butyl rubber containing sufficient amounts of bromine to improve its adhesive characteristics, and drying. 115

2. A process according to Claim 1, wherein the rubber latex is a butyl rubber latex.

3. A process according to Claim 1, wherein the rubber latex is a natural rubber 120 latex.

4. A process according to Claim 1, wherein the rubber latex is a polyhaloalkadiene rubber latex.

5. A process according to any of Claims 1 to 4 wherein the brominated butyl rubber contains at least 0.5 wt. % of combined bromine but not more than 3 combined atoms of bromine per double bond in the polymer. 125

6. A process according to any of Claims 130

- 1 to 5, wherein the brominated butyl rubber is in admixture with from 5 to 150 parts by weight per 100 parts by weight of said rubber of a filler.
- 5 7. A process according to any of Claims 1 to 6 wherein prior to coating the fibrous material, the phenolic-aldehyde resin-containing rubber latex is adjusted to a pH from 7 to 13 and aged at 40 to 150°F.
- 10 8. A process for improving the surface adhesion of a fibrous material according to Claim 1, substantially as hereinbefore described with particular reference to the examples.
- 15 9. Fibrous material treated by the process of any of the preceding claims.
10. A process for the production of a laminated structure comprising at least one layer of rubber and at least one layer of fibrous material comprising embedding the product of any of Claims 1 to 9 in an unvulcanized rubber matrix and vulcanizing *in situ* at an elevated temperature.
11. A process for the production of a laminated structure according to Claim 10, substantially as hereinbefore described with particular reference to the examples.
12. The laminated structure produced by the process of either of Claims 10 or 11.
13. A rubber tire which contains in the carcass layer thereof a plurality of cords embedded in a rubber, said cords having been coated according to the process of any of Claims 1 to 8.

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